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(54) PROCESS FOR PRODUCING POROUS CARBON

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a Japanese Body Corporate, of No. 15, Kitahama 5-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for producing porous carbon which is useful as a selective absorbent or separating agent.

It is known that some inorganic materials, such as porous glass, silica gel and porous silica bead, which have a narrow distribution of pore diameters, are useful as selective absorbents or separating agents. These inorganic materials selectively absorb and separate substances having a specific spread of molecular size from a mixture having various spreads of the molecules according to the distribution of pore diameter in the inorganic materials. However, these inorganic materials contain a polar group and hence are decomposed with an alkali or an acid, and therefore their use is limited within a specific area.

It is to be expected that porous carbon having a narrow distribution of pore diameter may be preferably used as an absorbent and separating agent without the defects of the conventional inorganic materials.

A process for producing a porous carbon material by activating carbon (e.g. charcoal) or a carbon precursor in an oxidative gas (e.g. steam) is known. However, in this process, it is very difficult to control the pore diameter because it is produced by decomposition, the mechanism of which is not clear. It is also known that porous carbon can be produced by binding carbon-containing material with a binder and then calcining the product, but in this process it is difficult to obtain carbon having a large pore volume. Other known processes comprise foaming thermosetting resins and then carbonising the resulting porous material. However, using these methods, it is difficult

to control the pore diameter and furthermore the product is inferior in mechanical strength because it has many closed cells.

It is also known that porous organic high molecular weight compounds can be produced by suspension-polymerizing a mixture of a monomer containing a plurality of non-conjugated ethylenically unsaturated groups and at least one monoethylenically unsaturated monomer in an aqueous medium in the presence of a precipitator which is a substantially water-insoluble liquid and functions also as the solvent for the mixture of the monomers and does not swell the resulting copolymer (Japanese Patent Publication No. 13792/1962). The present inventors have now found that the porous organic high molecular weight compounds thus obtained have a narrow distribution of pore diameter and a large pore volume and therefore have excellent mechanical strength, and that the desired porous carbon having a narrow distribution of pore diameter, a large pore volume and excellent mechanical strength can be produced from the porous organic high molecular weight compounds by making them infusible and then calcining them.

According to the present invention there is provided a process for producing porous carbon which comprises suspension-polymerizing a mixture of a first monomer, which contains a plurality of non-conjugated ethylenically unsaturated groups, and at least one other monomer, which is a monoethylenically unsaturated monomer in a liquid medium in the presence of a liquid precipitant which is substantially insoluble in the liquid medium, which functions as the solvent for the mixture of monomers and which does not swell the resulting copolymer, treating the resulting porous organic high molecular weight compound so as to make it infusible, and then carbonising the product.

The monomer containing a plurality of non-conjugated ethylenically unsaturated groups may be, for example, divinylbenzene, divinylpyridine, divinyltoluene, divinyl-

naphthalene, diallyl phthalate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, divinylxylene, divinylethylbenzene, divinylsulfone, glycol, glycerin, pentaerythritol, monothio or dithio derivatives of glycol, polyvinyl or polyallyl ether of resorcinol etc., divinyl ketone, divinyl sulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl tricarballoylate, triallyl aconitate, triallyl citrate, triallyl phosphate, N,N'-methylenediacylamide, N,N'-methylenedimethacrylamide, N,N'-ethylenediacylamide, 1,2-di(α -methylmethylenesulfonamido)ethylene, trivinylbenzene, trivinyl-naphthalene, or polyvinylanthracene.

The monoethylenically unsaturated monomer may be, for example, methyl acrylate or methacrylate, ethyl acrylate or methacrylate, propyl acrylate or methacrylate, isopropyl acrylate or methacrylate, butyl acrylate or methacrylate, tert-butyl acrylate or methacrylate, ethylhexyl acrylate or methacrylate, cyclohexyl acrylate or methacrylate, isobornyl acrylate or methacrylate, benzyl acrylate or methacrylate, phenyl acrylate or methacrylate, an alkylphenyl acrylate or methacrylate, ethoxymethyl acrylate or methacrylate, ethoxyethyl acrylate or methacrylate, ethoxypropyl acrylate or methacrylate, propoxymethyl acrylate or methacrylate, propoxyethyl acrylate or methacrylate, propoxypropyl acrylate or methacrylate, ethoxyphenyl acrylate or methacrylate, ethoxybenzyl acrylate or methacrylate, ethoxycyclohexyl acrylate or methacrylate, styrene, vinyltoluene, vinyl-naphthalene, and acrylonitrile. Monovinylidene compounds containing a nitrogen-containing heterocyclic group, such as vinylpyridine, 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, 2-methyl-3-ethyl-5-vinylpyridine, 2-methyl-5-vinylquinoline, 4-methyl-4-vinylquinoline, 1-methyl(or 3-methyl)-5-vinylisoquinoline or vinylpyrrolidone may also be used. A mixture of one or more of the above-listed monomers with a monovinylene compound (e.g. a dialkyl maleate, a dialkyl fumarate, a dialkyl crotonate, a dialkyl itaconate, or a dialkyl glutaconate) may be used.

The precipitant used in the invention should be substantially insoluble in the liquid medium and functions also as the solvent for the mixture of the monomers and does not swell the copolymer produced by the polymerization. The choice of a suitable precipitant may depend on the kind of monomer mixture used. For instance, when aromatic hydrocarbon monomers such as styrene and divinylbenzene are used, an

alkanol having from 4 to 10 carbon atoms may be preferable and can give the desired phase separation. The precipitant is preferably used in an amount of from 30 to 50% by weight on the basis of the whole weight of the monomers and the precipitant. For aromatic hydrocarbon monomers such as styrene and divinylbenzene, an aliphatic saturated hydrocarbon having at least 7 carbon atoms such as heptane, isooctane or the like may also be used as the precipitant. In this case the precipitant is preferably used in an amount of from 30 to 50% by weight on the basis of whole weight of the monomers and the precipitant.

When an acrylic acid ester is used as the monoethylenically unsaturated monomer, an alkyl ester having at least 7 carbon atoms may be useful as the precipitant. Representative examples of the alkyl esters are *n*-hexyl acetate, 2-ethylhexyl acetate, methyl oleate, dibutyl sebacate, dibutyl adipate and dibutyl carbonate. The amount of the alkyl ester may vary with the kinds of alkyl esters, but is usually from 30 to 50% by weight on the basis of whole weight of the monomers and the precipitant, in which amount the precipitant can effect the phase separation and the formation of net structure within the polymerization mass. When acrylic acid ester is used as the monoethylenically unsaturated monomer, an aliphatic saturated hydrocarbon having at least 7 carbon atoms, such as heptane, isooctane or the like may also be used as the precipitant, preferably in an amount of from 25 to 50% by weight on the basis of whole weight of the monomers and the precipitant.

When a monoethylenically unsaturated monomer containing a nitrogen-containing heterocyclic group such as vinylpyridine or a substituted vinylpyridine is used as the monoethylenically unsaturated monomer, an aliphatic saturated hydrocarbon having at least 7 carbon atoms is preferably used as the precipitant. Representative examples of suitable aliphatic saturated hydrocarbon are heptane and isooctane, which are preferably used in an amount of from 15 to 45% by weight on the basis of the whole weight of the monomers and the precipitant.

In the suspension polymerization in the present invention, there may be used a catalyst which can give a free radical and functions as the polymerization initiator. Suitable examples of the catalyst are benzoyl peroxide, tert-butyl hydroperoxide, cumene peroxide, tetralin peroxide (i.e. 1,2,3,4-tetrahydronaphthalene peroxide), acetyl peroxide, captoyl peroxide, tert-butyl perbenzoate, di-tert-butyl perphthalate and methyl ethyl ketone peroxide. The amount of the catalyst required may appropriately be parallel to the concentration of the mixture of the monomers, and may usually be 0.01 to 3%

by weight, preferably 0.2 to 1.5% by weight on the basis of the weight of the mixture of the monomers. The optimum amount of the catalyst may be determined by the properties of the monomers used (and also the properties of the impurities contained in the monomers).

Another suitable catalyst which can give a free radical is an azo compound. Suitable examples of azo compounds are azodiisobutyronitrile, azodiisobutylamide, azobis(α , α -dimethylvaleronitrile), azobis(α -methylbutyronitrile), and dimethyl, diethyl and dibutyl azobis(methylvalerate). These and other azo compounds, which have an -N-N- group bonded to an aliphatic carbon atom wherein at least one carbon atom is a tertiary carbon atom, can give rise to a free radical and use useful as polymerization initiators.

The catalyst may be used in an amount of 0.01 to 2% by weight on the basis of the weight of the starting monomers.

The polymerization of the monomers may also be carried out by irradiation using ultraviolet light at room temperature or a slightly higher temperature in the presence of an appropriate catalyst, such as benzoin, or azoisobutyronitrile.

A suspending agent, such as polyvinyl alcohol, ammonium salt of styrene-maleic anhydride copolymer, carboxymethyl cellulose, bentonite or magnesium silicate, may also be used in the suspension-polymerization of the invention.

When the medium is agitated during the suspension-polymerization, the phase containing the monomers is dispersed in the form of micro drops. The size of the drops may vary with various factors, such as the amount of the suspending agent, and the manner or speed of the agitation. The agitation is continued until the polymerization is completed. The polymerized drops, which are generally referred to as "beads", are separated from the suspension medium and may optionally be subjected to various other forms of subsequent treatment.

The suspension-polymerization of the monomers used in the present invention, e.g. the ethylenically unsaturated monomer or a mixture thereof, may preferably be carried out in an aqueous medium. However, when a water-soluble ethylenically unsaturated monomer is used, the aqueous medium is not used unless the monomer can be salted out.

As is well known, when oxygen is present in the polymerization system, the oxygen acts as an inhibitor of the free radical polymerization reaction and therefore should be removed. Accordingly, the suspension-polymerization of the present invention is preferably carried out under anaerobic conditions.

The porous organic high molecular weight compound thus obtained is made infusible by a conventional method, for instance, by treating it with oxygen, ozone, sulfur trioxide, sulfur dioxide, sulfuric acid, chlorosulfonic acid, nitrogen dioxide, nitrogen monoxide, chlorine, bromine, or hydrogen peroxide. The porous organic high molecular compound thus rendered infusible is calcined at a temperature greater than 500°C, preferably from 800 to 2800°C in an inert atmosphere (e.g. under nitrogen gas).

In the most preferable embodiment of the present invention, styrene-divinylbenzene copolymer is used as the copolymer and it is made infusible by treating with sulfur trioxide, sulfuric acid or chlorosulfonic acid.

When this preferred embodiment is employed, the copolymer is rapidly made infusible, the carbonisation of the infusible product is accomplished within a short time, and the desired carbon product having a narrow distribution of pore diameters can be produced in a high carbonization yield.

According to the present invention, the average pore diameter and the pore volume of the product can easily be controlled and the porous carbon obtained has a narrow distribution of pore diameters and excellent mechanical strength and therefore is useful as a selective absorbent or a separating agent in various industrial fields, for instance as a column packing agent for molecular weight fractionation.

The present invention is illustrated by the following Examples but is not limited thereto.

Example 1

Polyvinyl alcohol (5.0 g), carboxymethyl cellulose (1.7 g) and sodium chloride (56 g) were dissolved in distilled water (1.5 liter), and a mixture of styrene (200 g), divinylbenzene (a commercial product, purity: 55%, 55 g), 2 butanol (240 g) and benzoyl peroxide (1.5 g) was added to the solution. The resulting mixture was subjected to suspension-polymerization at 85°C for 6 hours with agitation to give a copolymer having a bulk density of 0.31.

The copolymer thus obtained (40 g) was sulfonated with 15% fuming sulfuric acid (500 g) at 110°C for 6 hours, washed with sulfuric acid and with water, and dried. The product was then carbonised by raising its temperature to 1000°C at a rate of 300°C/hour under nitrogen gas to give a porous carbon product having a bulk density of 0.44. The distribution of pore diameter was then measured by a mercury porosimeter (made by Carlo Erba) for the radius range of 50-75,000 Å and by a device using the N₂ desorption method (made by Carlo Erba) for the radius range of 20-50Å.

The accompanying Figure 1 shows the distribution of pore diameters of the styrene-divinylbenzene copolymer and of the porous carbon product obtained by making infusible and carbonising the copolymer.

Example 2

Polyvinyl alcohol (5.0 g), carboxymethyl cellulose (1.7 g) and sodium chloride (56 g) were dissolved in distilled water (1.5 liter), and a mixture of styrene (200 g), divinylbenzene (a commercial product, purity: 55%, 145.5 g) 2-butanol (230 g) and benzoyl peroxide (1.5 g) were added to the solution. The resulting mixture was allowed to react with agitation at 85°C for 6 hours to give a copolymer having a bulk density of 0.39.

The copolymer thus obtained (40 g) was sulfonated with 15% fuming sulfuric acid (500 g) at 110°C for 6 hours, washed with sulfuric acid and with water, and dried. The infusible product was then carbonised by raising its temperature to 1,000°C at a rate of 300°C/hour under nitrogen gas to give a porous carbon product having a bulk density of 0.55. The distribution of pore diameter of the porous carbon product is shown in the accompanying Figure 2.

For comparison purposes, the distribution of pore diameter of a commercially available activated carbon is also shown in Figure 2.

WHAT WE CLAIM IS:—

1. A process for producing porous carbon which comprises suspension-polymerizing a mixture of at least one first monomer, which contains a plurality of non-conjugated ethylenically unsaturated groups, and at least one other monomer, which is a monoethylenically unsaturated monomer in a liquid medium in the presence of a liquid precipitant which is substantially insoluble in the liquid medium, which functions as the solvent for the mixture of monomers and which does not swell the resulting copolymer, treating the resulting porous organic high molecular weight compound so as to make it infusible, and then carbonising the product.

2. A process as claimed in claim 1, wherein the liquid medium is an aqueous medium.

3. A process as claimed in claim 1 or claim 2, wherein the precipitant is an alkanol having from 4 to 10 carbon atoms, an aliphatic saturated hydrocarbon having at least 7 carbon atoms or an alkyl ester having at least 7 carbon atoms.

4. A process as claimed in claim 3, wherein the precipitant is used in an amount of from 30 to 50% by weight of the total weight of monomers and precipitant.

5. A process as claimed in claim 3 or claim 4, wherein the precipitant is heptane, isooctane, *n*-hexyl acetate, 2-ethylhexyl acetate, methyl oleate, dibutyl sebacate, dibutyl adipate, or dibutyl carbonate.

6. A process as claimed in any one of the preceding claims, wherein the porous organic high molecular weight compound is made infusible by treating it with oxygen, ozone, sulfur trioxide, sulfur dioxide, sulfuric acid, chlorosulfonic acid, nitrogen dioxide, nitrogen monoxide, chlorine, bromine, or hydrogen peroxide.

7. A process as claimed in any one of the preceding claims, wherein the carbonisation of the infusible porous organic high molecular weight compound is carried out by heating it at a temperature of more than 500°C in an inert atmosphere.

8. A process as claimed in claim 7, wherein the carbonisation is carried out at a temperature of from 800 to 2,800°C.

9. A process as claimed in any one of the preceding claims, wherein the first monomer is divinylbenzene, and the other monomer is styrene.

10. A process as claimed in claim 9, wherein sulfonation is carried out using sulfur-trioxide, sulfuric acid, or chlorosulfonic acid and carbonisation is carried out under nitrogen.

11. A process for producing porous carbon substantially as hereinbefore described in Example 1 or Example 2.

12. Porous carbon when produced by a method as claimed in any one of the preceding claims.

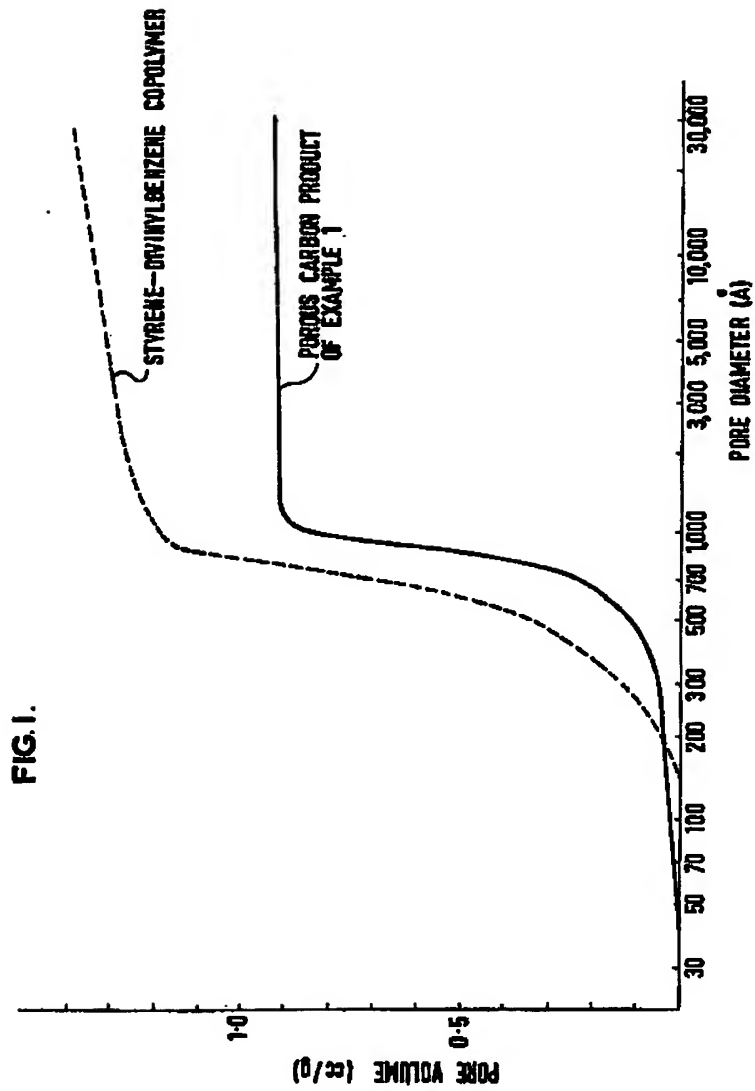
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FIG. 2.

